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Structure evolution and magnetic properties of annealed nanoscale Gd/Ti multilayers

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Abstract. The structure and magnetic properties were comparatively analyzed for $[Gd/Ti]_n$ multilayers with Gd layer thickness of 1.5 to 12 nm. Multilayers were deposited by sputtering technique at room temperature and annealed for the temperatures up to 400 ºC. It was observed that the samples are highly textured in a different way depending on the Gd layer thickness and annealing temperature. It was found that the heat treatment practically does not change the Gd grain size. The lattice parameters obtained from X-ray results change significantly only for $[Gd(1.5nm)/Ti]_{50}$ multilayers, but their values remain higher than for the bulk Gd. The initial slope of the temperature dependence of magnetization near Curie temperature becomes steeper and Curie temperature increases upon annealing. Curie temperature variation can be understood by taking into account both relaxation of the lattice imperfections and change in lattice constants.

1 Introduction

Magnetic properties of nanostructured ferromagnetic materials show strong dependence on the microstructure [1]. This connection is important both in fundamental and applied science. For example, nanostructured Gd has different magnetocaloric behavior when compared with the bulk counterparts [2-4]. The common way to characterize the magnetocaloric effect of a magnetic material is the relative cooling power (RCP), which is defined as the product of the maximum isothermal entropy change, $\Delta S_{mag}(T,H)$, during the magnetization process, and the corresponding full-width-at-half-maximum (δT_{FWHM}), and Curie temperature (T_C), which establishes the optimal operating temperature [5]. The practical utility of using the average nanocrystallite size and size distribution as control parameters to tune the magnetocaloric effect was recently demonstrated: the isothermal change in magnetic entropy at T_C caused by an applied magnetic field is greater in bulk ferromagnets than in their nanocrystalline counterparts. However, the reduction in the maximum ΔS_{mag} is offset by an appreciable increase in δT_{FWHM} due to the distribution of Curie temperatures in nanocrystalline systems [4]. It is also interesting to point out that the development of magnetocaloric materials with a distribution of Curie temperatures can be used to enhance the magnetic field responsiveness of these materials in the field range appropriate for technological applications. In these cases, ΔS_{mag} has a linear dependence with a magnetic field (H) in a broad temperature range close to the transition temperature, which is an enhancement with respect to the typical $H^{0.7}$ behavior of bulk materials [6]. Moreover, in terms of the magnetocaloric effect, not only the T_C value, but also the magnitude of the derivative of the magnetization with respect to temperature at a constant magnetic field near T_C is very important [7].

It is known, that Curie temperature of nanocrystalline gadolinium depends on the grain size and therefore annealing is an effective way to change the grain size and T_C as a consequence [8]. The data and interpretations reported up to now in the literature with respect to the Gd films are not consistent. The influence of annealing on the T_C value was observed in the relatively thick films (L_{Gd} = 0.9 μm) [9]. At the same time T_C was not changed in the case of thin films (L_{Gd} ~ 100 nm) for the heat treatments up to 300 ºC [10]. In addition, for L_{Gd} below ~ 5 nm, there is a sharp decrease in T_C [11, 12], according to the well known size effect [13].

Magnetron sputtering deposition of nanoscale Gd multilayers is a simple way to get gadolinium in nanocrystalline state. For any variation of Gd layer thicknesses the average size of Gd grain was always observed to be less than in "bulk" nanocrystalline Gd. Moreover, controlled heat treatment is an additional way to change the structure of the multilayered samples toward a desired state.

In this work the structure and magnetic properties were comparatively analyzed for $[Gd/Ti]_n$ nanoscale multilayers prepared by dc magnetron sputtering.

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2 Experimental

The Gd/Ti multilayers were prepared by alternative dc magnetron sputtering deposition of Gd layers and Ti spacers onto glass substrates. The base pressure in the chamber was 3×10^{-7} mbar and argon gas pressure of 3×10^{-3} mbar was used during the sputtering process. The deposition rate was 0.15 nm/s for Gd and 0.07 nm/s for Ti layers. The thicknesses of the Gd layers were varied from 1.5 nm to 12 nm and the thickness of Ti non-magnetic spacers was kept constant (2 nm). For comparison, a relatively thick single layer Gd film with L_{Gd} = 290 nm was also prepared. Ti was chosen for the spacers on the basis of its low solubility in rare earth materials. Each sample had a protective buffer and coating layers.

The microstructure of the samples was studied by X-ray diffraction (XRD) using CuK_α radiation. The annealing of the samples was performed in the X-ray diffractometer chamber in vacuum of 10^{-5} mbar. The sample was kept at annealing temperature for 1 hour, it was cooled down to room temperature at which the corresponding X-Ray spectra were also recorded. Low angle XRD was used to determine the quality of the layers. Magnetization (M) measurements with temperature were performed with the VSM magnetometer. T_C was taken from the inflection point in the $M(T)$ curve, above which the magnetization is dominated by the paramagnetic tail caused by the applied field.

3 Results and discussion

According to the XRD data, the studied samples are polycrystalline with mainly an equilibrium hcp phase. They have a strong texture: only selected peaks are clearly visible in the XRD patterns (figure 1). For the most part of the relatively thick single layer Gd film, the (100) plane is parallel to the substrate surface. The L_{Gd} decrease leads to (002) preferred orientation. Moreover, for Gd (290nm) film the presence of fcc phase was detected from a broad peak at $2\theta \approx 28.7°$ (figure 2). This metastable fcc phase was observed previously in thin Gd films by other authors [14, 15]. The amount of fcc Gd decreased continuously with increase of the annealing temperature, and almost disappears following the annealing treatment at 400 ºC. The lattice constants obtained from the fit for Gd (290nm) film are **a** = 3.62 Å and **c** = 5.78 Å for the hcp structure in as-deposited state. These values agree with those for the bulk Gd. The heat treatment slightly reduces the lattice constants (**a** = 3.60 Å and **c** = 5.74 Å after annealing at 400 ºC), but **c**/**a** ratio remains almost unchanged, **c**/**a** = 1.59.

It seems that for [Gd(3nm)/Ti]$_{30}$ multilayers the peak around 31-32° is a combination of the hcp (002) and the hcp (101) reflections (figure 3). Relative intensity of the hcp (002) peak increases with annealing temperature, but location of both peaks remains unchanged. The lattice constants obtained from the fit are **a** = 3.66 Å and **c** = 5.80 Å, and **c**/**a** ratio little less than for the bulk Gd, **c**/**a** = 1.58.

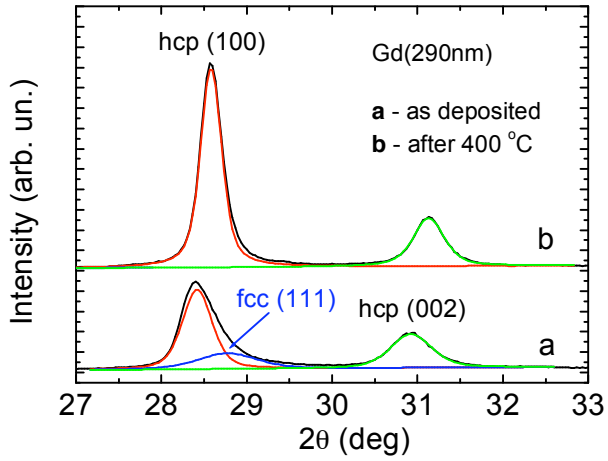

Fig. 2. X-ray diffractograms for Gd(290nm) film immediately after deposition (a) and after annealing at 400 ºC (b). The fit is an overlap of three different functions (red, blue and green lines).

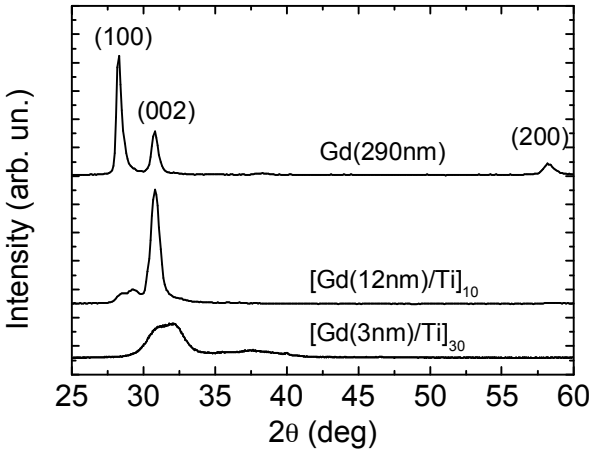

Fig. 1. X-ray diffractograms for Gd(290 nm) film, [Gd(12 nm)/Ti]$_{10}$ and [Gd(3 nm)/Ti]$_{30}$ multilayers in initial state (immediately after deposition).

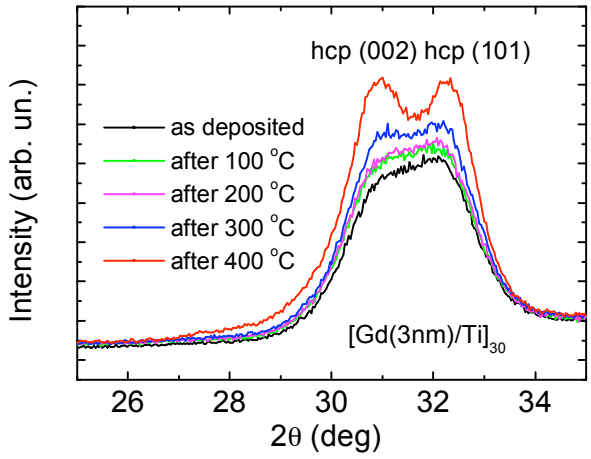

Fig. 3. X-ray diffractograms for [Gd(3nm)/Ti]$_{30}$ multilayers immediately after deposition and after annealing at different temperatures.

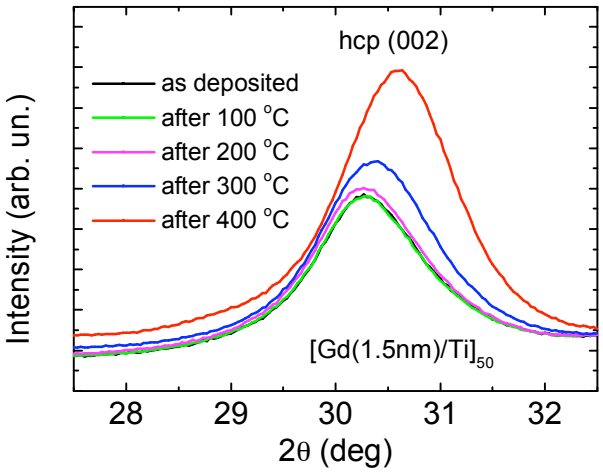

Fig. 4. X-ray diffractograms for $[Gd(1.5nm)/Ti]_{50}$ multilayers immediately after deposition and after annealing at different temperatures.

The XRD patterns for $[Gd(1.5nm)/Ti]_{50}$ multilayers are characterized by only one intensive maximum at $2\theta \approx 30.5°$ position (figure 4). It can be due to the preferential orientation of the (002) planes of hcp Gd. The peak position was displaced with annealing temperature. The lattice parameter **c** obtained from these date decreases with annealing treatment from 5.90 to 5.84 Å, but its value remains higher than for the bulk Gd.

The low angle XRD patterns for all multilayers showed Bragg peaks associated with the periodic structure of the multilayers. The observed peaks allow the determination of the layer thickness which agrees well with that expected from the deposition time. Both the presence of the peaks and their almost unchanged position indicate that the heat treatment has not disrupted the layered structure of the samples. Figure 5 shows an example of the low-angle X-ray diffractograms for the $Gd(3nm)/Ti]_{30}$ sample.

In all cases the grain size was calculated using the Scherer formula for (002) reflection [16]. For Gd (290nm) film the grain size insignificantly increases from 20 to 25 nm with the heat treatment.

For multilayers with L_{Gd} 12 nm and 6 nm, the Gd grain size was estimated as equal to the thickness of the Gd layers. For the samples with L_{Gd} of 3 nm and 1.5 nm, the Gd grain size was 5-7 nm, approximately. This means, that in multilayers with $L_{Gd} < 6$ nm the grains are elongated in the plane direction. Heat treatment practically did not change the grain size in the multilayers. An indirect confirmation of this fact is the low-angle X-ray spectra shape preserving (figure 5).

Figure 6 shows an example of the temperature dependence of normalized magnetization of the Gd(290nm) film and $Gd(3nm)/Ti]_{30}$ multilayers for different annealing stages. This dependence allows us to observe the change in the slope of magnetization curves and shift of T_C. For all samples annealing at $T_{ann} = 100$ °C already changes magnetization curves: the initial slope of the magnetization is steeper and T_C shifts slightly to the bulk T_C. Annealing yields qualitatively the same results for the higher T_{ann}: the initial slope near T_C becomes steeper, or, in other words, the transition becomes sharper.

The values of T_C are shown in figure 7 as a function of annealing temperature. For the samples with $L_{Gd} > 3$ nm there is almost linear increase of the T_C with annealing temperature. For Gd(290nm) film T_C rises to about 293 K, i.e. up to the value characteristic for the

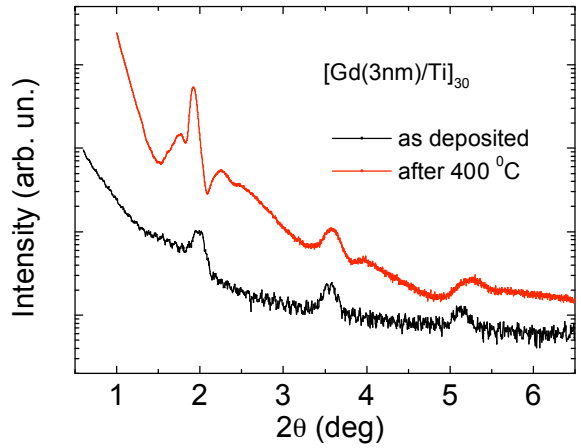

Fig. 5. Low angle X-ray diffraction for $[Gd(3nm)/Ti]_{30}$ multilayers immediately after deposition and after annealing at 400 °C.

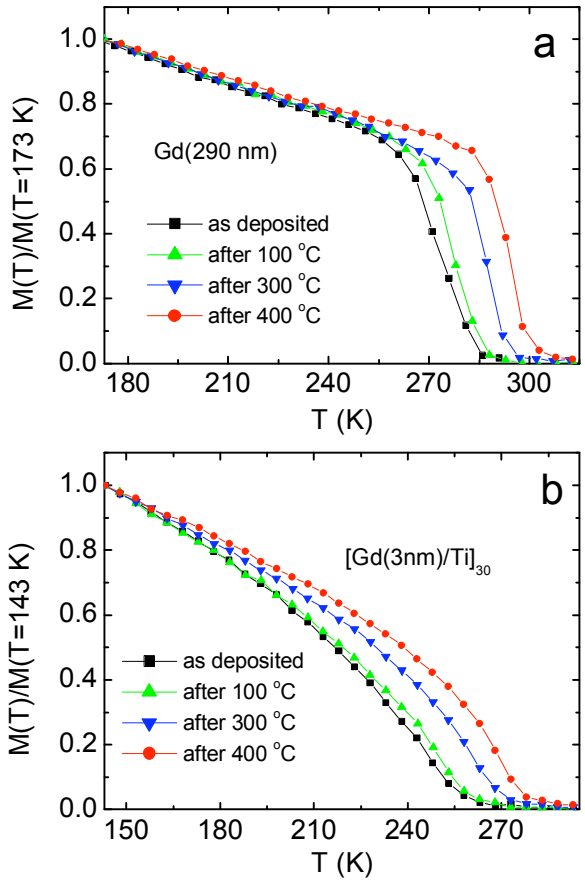

Fig. 6. Normalized magnetization for Gd(290nm) film (a) and $[Gd(3nm)/Ti]_{30}$ multilayers after different annealing steps. Measuring field is 120 Oe.

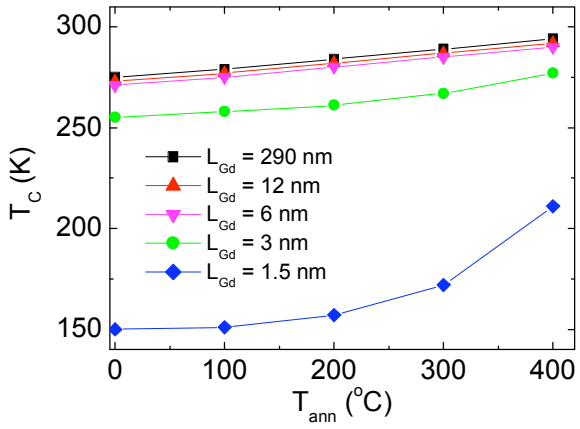

Fig. 7. Curie temperatures T_C as functions of annealing temperature T_{ann} for the samples with different thickness of Gd layers. Measuring field is 120 Oe.

bulk Gd. The absolute T_C value is different for these samples due to the finite size effect [12]. For the $[Gd(3nm)/Ti]_{30}$ sample at $T_{ann} > 200$ °C a more intensive T_C increase was observed. This tendency become even more pronounced in the case of $[Gd(1.5nm)/Ti]_{50}$ multilayers.

The following reasons can explain the changes of T_C with annealing for Gd/Ti multilayers: a change of grain size [8], change in lattice constants [17] and relaxation of lattice imperfections [9]. Since the exchange integral in Gd depends sensitively on interatomic distances, all mentioned factors may results in the reduction of Curie temperature [18]. Taking into account X-ray data, which indicate that the grain size is practically unchanged and the lattice constants shows visible changes only in the case of the most thin Gd layers, one can make a supposition about the main reason of the T_C variation for Gd/Ti multilayers. For $L_{Gd} > 1.5$ nm it is a relaxation of lattice imperfections, which are usually incorporated in the films prepared with a sputtering method. This mechanism also plays a decisive role in the case of $[Gd(1.5nm)/Ti]_{50}$ multilayers, but the change in the lattice constants is probably even more important. For these multilayers significant changes in the lattice parameter **c** were observed, being in a good agreement with the fact that T_C is very sensitive to the change of the lattice constants [17].

4 Conclusion

$[Gd/Ti]_n$ multilayers were prepared by dc magnetron sputtering. The thicknesses of the Gd layers were varied in the range of 1.5 nm to 12 nm. The samples were stepwise annealed up to 400 °C in the X-ray diffractometer chamber in vacuum of 10^{-5} mbar. Comparative analysis of the effects of annealing temperature on the structure and magnetic properties was done. The annealing treatment practically does not influence the Gd grain size. The changes of the lattice parameters are noticeable at $L_{Gd} < 6$ nm. The initial slope of the $M(T)$ near T_C becomes steeper and T_C value increases upon annealing. Both relaxation of lattice imperfections and change in lattice constants are the reasons of the T_C change. Thus, the Curie temperature and the initial slope of the temperature dependence of magnetization near T_C of sputtered Gd thin films and multilayers can be suitably altered by variation of Gd layer thickness and the after deposition annealing.

Acknowledgments

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